

Reactive Extrusion of Starch–Polyacrylamide Graft Copolymers Using Various Starches

J. L. Willett · V. L. Finkenstadt

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Abstract Graft copolymers of polyacrylamide and various substrates were prepared by reactive extrusion in a twin screw extruder using ammonium persulfate as initiator. Substrates included unmodified starches (corn, waxy maize, wheat, and potato), cationic starches, dextrin, dextran, and polyvinyl alcohol (PVOH). The feed ratio of substrate to monomer was 2:1. Average conversion of monomer to polymer was 88.9% ($\pm 5.1\%$). Graft contents for the starch substrates were approximately 25% with grafting efficiencies of about 70%. Polyacrylamide graft molecular weights ranged from 317,000 to 769,000. Absorbencies at pH 7 for saponified graft copolymers prepared with unmodified starches were approximately 200 g/g and approximately 150 g/g for the cationic starches, dextran, and PVOH. In electrolyte solution (0.9% NaCl), absorbencies were in the range of 26–59 g/g, depending on substrate type. Saponified dextrin copolymers were essentially soluble with absorbencies of 6 g/g in water and 12 g/g in 0.9% NaCl.

Keywords Starch · Graft copolymer · Reactive extrusion · Polyacrylamide

Introduction

The development of starch-based superabsorbents by USDA researchers in the 1970s [1, 2] stimulated considerable interest in these materials. A variety of monomers, substrates, initiators, and other additives have been reported [3–9]. Potential applications of starch-based superabsorbents include personal care products, fire-fighting gels, and agricultural uses.

Processing of most starch-based graft copolymers typically involves a series of batch processes and consumes large quantities of water [10, 11]. Reactive extrusion has been explored as an alternate process for continuous production of starch graft copolymers with reduced water requirements [12, 13]. Carr et al. [13] demonstrated that starch–polyacrylonitrile graft copolymers prepared by reactive extrusion could, after saponification, absorb approximately 300 times their weight in water.

Recently we have shown that starch–polyacrylamide graft copolymers can be produced with high conversion and grafting efficiency using a corotating twin screw extruder [14, 15]. Here we report the production of polyacrylamide (PAAm) graft copolymers using various unmodified and modified starches, as well as dextrin, dextran, and polyvinyl alcohol as substrates. After saponification, absorbencies were measured at pH 7 in deionized water and 0.9% NaCl solution.

Materials and Methods

The substrates for graft copolymerization are listed in Table 1. Starches used were corn starch (Pure Food Powder), waxy maize (Waxy 7350), cationic corn (Stalok 300), and cationic waxy maize (Stalok 180), all obtained from

Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

J. L. Willett (✉) · V. L. Finkenstadt
Plant Polymer Research Unit, U.S. Department of Agriculture,
Agricultural Research Service, National Center for Agricultural
Utilization Research, Peoria, IL 61604, USA
e-mail: willettjl@ncaur.usda.gov

Tate and Lyle NA; potato starch (Avebe); and wheat starch (Midsol 50, Midwest Grain Products). Other polysaccharide substrates were corn starch dextrin (Stadex 9, Tate and Lyle NA) and dextran (grade 2P, Pharmachem Corp.). The dextrin is a low conversion, partially hydrolyzed starch product with approximately 10% water solubles. Dextran is a branched polysaccharide with primarily 1,6-linked α -D-glucose units in the chain backbone. Poly(vinyl alcohol) (Airvol 523S, Air Products) was used as a synthetic hydroxyl-rich substrate. Ammonium persulfate (Aldrich) and acrylamide (50 wt% solution, Cytec Ind.) were used as received.

Reactive extrusion was performed using a Werner-Pfleiderer ZSK-30 corotating twin screw extruder. Details of the extruder and screw configuration have been presented elsewhere [14]. The extruder barrel consisted of 14 barrel sections, with eight independent temperature control zones. Barrel temperature set-points were 80/90/90/90/110/110/100/80 °C. Feed rates were adjusted to give substrate/acrylamide ratio of 2:1 (solids basis) with water content of 50% at a total feed rate of 12.1 kg/h. Solid substrates with ambient moisture were fed gravimetrically. Liquids were fed using triple piston metering pumps (Eldex); rates were monitored by following weight loss of reservoir containers. Ammonium persulfate (5 wt% solution) was fed at a rate to give 1% by weight based on the starch. This corresponds to approximately 70 anhydroglucose units per initiator radical for the polysaccharide substrates and approximately 250 PVOH repeat units per radical. Extrudates were collected for approximately 15 s, yielding samples of approximately 50–60 g. To quench the polymerization, extrudates were immediately dispersed in ethanol with 0.5 wt% hydroquinone, followed by steeping overnight to remove unreacted monomer. Solids were collected by filtration and dried.

Nitrogen contents (wt% N) were measured in triplicate using a Perkin–Elmer 2400 Series II Dumas-type H/C/N analyzer. Monomer conversion was determined by the ratio of the nitrogen content in the quenched extrudate to the nitrogen content in the feed (calculated using measured feed rates). Homopolymer PAAm was extracted from

quenched samples by stirring overnight at room temperature in a water/ethanol solvent (70/30 w/w). Graft contents and graft efficiencies were calculated based on nitrogen content after extraction [14]. Graft frequencies (N_{AGU}), in anhydroglucose units (AGU) per graft, were calculated as described previously [14].

Starch was removed from extracted graft copolymers by enzyme hydrolysis prior to molecular weight determination. Approximately 100 mg of copolymer were dispersed in 100 mL hot distilled water. Pullulanase and α -amylase (Megazyme) were added in excess, and the mixture (pH=6) was digested overnight with gentle agitation. Complete hydrolysis of starch to glucose was confirmed by thin layer chromatography. It was not possible to remove the dextran or the PVOH using this procedure, and PAAm molecular weights are not reported for these samples.

Polyacrylamide molecular weights (weight average) were determined by gel permeation chromatography using Shodex 804 and 806 columns in series with polyacrylamide standards (Polysciences). Flow rate of the mobile phase (0.1% NaNO₃) was 0.8 mL/min at a column temperature of 45 °C. Aliquots of the starch digestions were injected without further purification. Data acquisition and analysis were performed using ChromQuest and Polymer Labs GPC RE-analysis software, respectively.

Unextracted graft copolymers were saponified by placing 0.50 g in a 25 mL Erlenmeyer flask and adding deionized water to wet the sample. KOH solution (0.23 N) was added with stirring to give a molar ratio of KOH to acrylamide groups of 0.8. Total volume (water and KOH solution) was 12 mL. The flasks were heated in a water bath for 15 min, capped lightly to allow venting, and placed in a forced air oven at 95 °C. After 1 h, the samples were removed and cooled to room temperature. HCl (3 N) was added to lower the pH to about 7. The saponified sample was precipitated in 30 mL ethanol, stirred for 30 min, and filtered. The solids were dispersed in 15 mL of 90/10 ethanol/water, broken into small pieces with a stirring rod, and filtered while rinsing with the ethanol/water. Rinsed solids were dried overnight in a circulating air oven at 60 °C. Saponified materials were screened, and fractions collected from mesh sizes of +80, +120, and +170. Absorbencies were measured in duplicate for each size fraction by dispersing approximately 10 mg saponified copolymer in 10 mL deionized water (pH 7) or 0.9% NaCl solution. Samples were steeped with occasional swirling for 1 h. Gels were filtered on a tared 230 mesh screen sieve, tilted at an angle of approximately 15° to aid drainage of free water. After 30 min, the sieve was tilted the opposite way for another 30 min, then weighed. Absorbencies are reported as grams gel per gram saponified graft copolymer. Since screen size had no discernible effect on absorbency, the averages reported are from six measurements.

Table 1 Substrates for graft copolymerization with acrylamide

Substrate	Nitrogen content (wt%)	Moisture content (wt%)
Normal corn starch	0.14	10.0
Waxy maize starch	0.00	11.5
Wheat starch	0.05	9.4
Potato starch	0.05	9.9
Cationic normal corn starch	0.22	11.0
Cationic waxy maize starch	0.26	10.7
Dextrin	0.00	9.1
Dextran	0.09	8.6
Polyvinyl alcohol	0.00	4.2

Results and Discussion

Graft parameters

Properties of the graft copolymers are given in Table 2. The average conversion of acrylamide monomer to polyacrylamide (PAAm) was 88.9% ($\pm 5.1\%$) independent of substrate type. Wheat starch had the lowest conversion (80.9%) while the dextran gave the highest (98.5%). The conversion values are consistent with our previous results for reactive extrusion of unmodified corn and waxy maize starches at comparable starch/acrylamide feed ratios, and indicate that the reaction time scale is of the same order or less than the residence time (less than ≈ 400 s) [14].

Graft content is the amount of PAAm remaining after extraction with aqueous ethanol. As shown in Table 2, the average graft content for the starch substrates was 26.2% ($\pm 1.6\%$). Graft content of the dextrin copolymer (26.8%) was equivalent to that of the starch materials, while graft content of the dextran copolymer (32.5%) was significantly greater. The PVOH-g-PAAm copolymer had a graft content of 28.2%.

Graft efficiency is the ratio of insoluble (grafted) PAAm to the total amount of PAAm formed. As seen in Table 2, graft efficiencies for the starches were 75% or greater. Cationic modification did not significantly affect grafting efficiency. Grafting efficiencies for the waxy maize starches were somewhat lower than those for the corn starches, consistent with results observed previously [14]. Grafting efficiency for the dextran was 67.8%, comparable to the values for the starch substrates. Dextrin gave a grafting efficiency less than 30%, due in part to the high solubility of this substrate in the aqueous ethanol extraction solvent, as shown in Table 3.

After extraction, starch was removed by enzymatic hydrolysis and the remaining PAAm analyzed by GPC. As shown in Table 2, molecular weights of the grafted PAAm ranged from 317,000 to 769,000 depending on substrate. Of the unmodified starches, normal corn and waxy maize starches gave the highest molecular weights, while wheat

starch and potato starch were essentially equal. The source of this difference is not clear. The cationic starches yielded PAAm molecular weights which were significantly lower than any of the unmodified starches, suggesting that the cationic modification may increase chain transfer to the starch. PAAm isolated from the dextrin copolymers had molecular weight comparable to that of the unmodified corn starches. Since neither dextran nor PVOH were susceptible to enzymatic hydrolysis, grafted PAAm from these samples could not be isolated by this method. The aqueous extract of the PVOH-g-PAAm copolymer showed two peaks in the GPC trace (data not shown): a lower molecular peak corresponding to the starting PVOH ($M_w \approx 65,000$), and a smaller peak at higher molecular, presumable due to the graft copolymer. This peak had an elution time comparable to that of the PAAm from the cationic waxy maize starch copolymer.

Graft frequencies, defined as the number of anhydroglucose units between grafts (N_{AGU}), are also shown in Table 2. The unmodified starches and dextrin have graft frequencies between 5000 and 7000, with the corn starches giving slightly higher values than wheat or potato starch. Graft frequencies for the modified corn starches are significantly lower than those for the unmodified starches. It is interesting that the cationic starches appear to give copolymers with more grafts of lower molecular weight compared to the unmodified starches, even though the conversion and grafting efficiencies are essentially the same. Cationic modification apparently promotes chain transfer to starch, which would decrease both the PAAm molecular weight and N_{AGU} .

As shown in Table 3, graft copolymers using the unmodified normal corn, wheat, and potato starches gave aqueous ethanol solubles of approximately 10%, which were roughly one-half polyacrylamide and one-half carbohydrate. Comparable results were obtained with the cationic NCS, with a soluble fraction of 12.8% which was 46% PAAm. The cationic waxy maize starch had higher solubility (21.2%) than the other starches, although the soluble PAAm content was similar (42.1%). The dextran-PAAm

Table 2 Properties of graft copolymers

Substrate	Conversion (%)	Graft content (wt%)	Graft efficiency (%)	PAAm molecular weight ($\times 10^{-3}$)	Graft frequency N_{AGU}
Normal corn starch	84.3	24.7	82.3	769	7040
Waxy maize starch	90.7	26.2	75.3	699	6080
Potato starch	90.4	26.3	83.6	550	5150
Wheat starch	80.9	24.6	80.6	583	4990
Normal corn starch (cat.)	90.1	29	87.4	457	3320
Waxy maize starch (cat.)	91.9	26.3	70.9	317	2600
Dextrin	88.6	26.8	29.3	725	6110
Dextran	98.5	32.5	67.8	—	—
Polyvinyl alcohol	82.5	28.2	26.3	—	—

—, not determined

Table 3 Solubility data for graft copolymers in 30/70 ethanol/H₂O

Substrate	Solubles (wt%)	PAAm in solubles (wt%)
Normal corn starch	9.2	57.7
Waxy maize starch	14.0	53.6
Potato starch	10.0	46.6
Wheat starch	9.2	63.8
Cationic normal corn starch	12.8	46.0
Cationic waxy maize starch	21.2	42.1
Dextrin	68.0	32.7
Dextran	32.8	35.0
Polyvinyl alcohol	72.8	29.6

graft copolymer was 32.8% soluble, with a PAAm content of 35% indicating a larger soluble carbohydrate fraction compared to the starches. The higher graft content of the dextran graft copolymer may therefore be due in part to the higher carbohydrate solubility of this material compared to the starch substrates. The dextrin copolymer was highly soluble in aqueous ethanol (68.0%), with the soluble fraction having a carbohydrate/PAAm composition of roughly 2:1. The PVOH copolymer was also highly soluble in aqueous ethanol (72.8%).

Processing parameters

Extrusion data are listed in Table 4. Specific mechanical energy (SME) is a measure of the mechanical energy imparted to the material during extrusion, and is an important parameter in starch extrusion [16]. Die pressure is related to the viscosity of the extrudates. For a given starch, SME and die pressure are correlated with the AAm/starch feed ratio [14, 15].

There are significant differences in SME and die pressure between the substrates. SME values for the corn starch graft copolymers are approximately 375 kJ/kg, except for the cationic waxy maize starch which is 277 kJ/kg. Copolymers with the unmodified corn starches had greater die pressures than the corresponding modified starches, indicating greater

viscosities. The wheat starch copolymer was comparable to the corn starch in die pressure and SME. The potato starch copolymer had the largest SME (557 kJ/kg) and die pressure (1.64 MPa) of the starches used. As expected, die pressure (0.39 MPa) and SME (65 kJ/kg) for the dextrin copolymer were significantly lower, reflecting the lower molecular weight of this substrate.

When dextran was used as the substrate, SME (597 kJ/kg) was significantly greater than values obtained with any of the starches, while the die pressure (0.89 MPa) was comparable to that of the cationic waxy maize starch. The dextran SME values were comparable to those seen in previous extrusion of this polymer [17].

Graft copolymer prepared using the PVOH substrate gave the highest die pressure (2.12 MPa) of all the substrates used. SME (495 kJ/kg) was greater than all of the starches except potato starch. The greater die pressure of the PVOH graft copolymer is likely related to the linear nature of this substrate compared to the highly branched amylopectin in the starches.

There is no correlation between the grafting parameters and either SME or die pressure when comparing the different substrates. It therefore appears that the polymerization and grafting mechanisms of the acrylamide-persulfate system are relatively insensitive to the rheological properties present during reactive extrusion with starches, dextran, and PVOH.

Saponification and absorbency

Saponification of starch–PAAm graft copolymers with alkali converts a portion of the acrylamide units to anionic carboxylate groups. As shown in Table 5, the saponification procedure converted approximately 45% of the acrylamide units in the unextracted materials. The PVOH graft copolymer was saponified to a significantly lower extent for reasons that are not clear.

Absorbencies of the saponified materials are also given in Table 5. There is some scatter in the data, with coefficients of variance between 15% and 20% in most cases. In DI water, absorbencies of the unmodified starches are between 190 and 253 g/g. Absorbencies of the graft copolymers prepared using the cationic starches are somewhat lower, with no difference between the two starch types. Dextran and PVOH copolymers gave absorbencies comparable to those of the cationic starches. Saponified dextrin graft copolymers, however, were essentially soluble in DI water; the small fraction which remained on the sieve gave an absorbency of 6 g/g.

In the presence of electrolyte (0.9 wt% NaCl), electrolyte screening significantly reduced absorbencies compared to those in DI water as shown in Table 5. Absorbencies for the starch copolymers range from 45 to 60 g/g. Analysis of

Table 4 Specific mechanical energy and die pressure

Substrate	Specific mechanical energy (kJ/kg)	Die pressure (MPa)
Normal corn starch	365 (6)	1.43 (0.03)
Waxy maize starch	380 (5)	1.16 (0.03)
Potato starch	557 (14)	1.64 (0.06)
Wheat starch	388 (8)	1.52 (0.05)
Cationic normal corn starch	390 (21)	1.47 (0.03)
Cationic waxy maize starch	277 (7)	0.80 (0.03)
Dextrin	65 (3)	0.39 (0.03)
Dextran	597 (15)	0.89 (0.03)
PVOH	495 (8)	2.12 (0.15)

Table 5 Properties of saponified graft copolymers

Substrate	Degree of saponification (%)	Absorbency (DI water)	Absorbency (0.9% NaCl)
Normal corn starch	40.9	201 ^a (21)	59 ^a (12)
Waxy maize starch	43.8	253 ^b (31)	54 ^a (9)
Potato starch	39.4	190 ^{ac} (22)	54 ^a (13)
Wheat starch	44.3	226 ^{abc} (27)	45 ^{ab} (2)
Cationic normal corn starch	42.8	156 ^{acd} (26)	49 ^a (8)
Cationic waxy maize starch	46.5	154 ^{acd} (17)	55 ^a (14)
Dextrin	32.6	6 ^c (1)	12 ^d (4)
Dextran	46.2	144 ^{cd} (33)	26 ^{cd} (4)
PVOH	6.0	139 ^d (34)	30 ^{bc} (3)

Absorbency=gram gel/gram dry copolymer

Standard deviations are given in parentheses

Values with the same letter in a column are not significantly different at the 0.05 level

variance indicates no significant differences between any of the starches ($p=0.05$). As in DI water, absorbencies for the dextran (26 g/g) and PVOH (30 g/g) copolymers are somewhat lower those of the starches. The dextrin copolymer gives an absorbency of only 12 g/g, comparable to the value obtained in DI water. The low absorbency values for the dextrin copolymer suggest that little crosslinking occurs during reactive extrusion, consistent with the tendency of PAAm to terminate by disproportionation rather than coupling [18].

Comparison of the data in Tables 2 and 5 suggests some degree of correlation between graft frequency and absorbency in DI water for the starch substrates, with larger N_{AGU} values giving higher absorbencies. Given the standard deviations in the absorbency values, it is not clear that this correlation is significant. No correlation is observed when absorbency is measured in 0.9% NaCl. These results suggest that the presence of high molecular weight starch is needed to provide absorbency since the saponified dextrin copolymers are essentially soluble. The weak correlation between N_{AGU} and absorbency in DI water suggests that selection of extrusion and formulation parameters which yield graft copolymers with fewer grafting sites will give larger absorbencies. Further research is needed to clarify this correlation.

Conclusion

Graft copolymers with polyacrylamide with several polysaccharide substrates and polyvinyl alcohol were prepared using reactive extrusion. Average conversion of monomer was 88.9% and showed no dependence on substrate. Graft contents were approximately 25% with grafting efficiencies of 70% or greater in most cases. Molecular weights of grafted polyacrylamide ranged from 317,000 to 769,000 and were highest with unmodified starches. After saponification, absorbencies in deionized water (pH 7) ranged from 150 to 250 g/g. Absorbencies in electrolyte solution (0.9 wt% NaCl) ranged from 45 to 60 g/g for the starch graft copolymers, with unmodified starches giving the highest absorbencies. Saponified graft copolymers with dextrin, a hydrolyzed starch product, were essentially soluble with an absorbency of 6 g/g.

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